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Improved bioactivity properties of SiO_2-CaO-P_2O_5 glasses by using calcium L-lactate pentahydrate as calcium oxide precursor

G. Țăran[a], K. Magyari[b,*], A. Topan[a], A. Vulpoi[b], L. Baia[a,b,**]

[a] Faculty of Physics, Babes-Bolyai University, M. Kogalniceanu 1, 400084 Cluj-Napoca, Romania
[b] Nanostructured Materials and Bio-Nano-Interfaces Center, Interdisciplinary Research Institute on Bio-Nano-Sciences, Babeș-Bolyai University, M. Kogalniceanu 1, 400084 Cluj-Napoca, Romania

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ABSTRACT

In this work, SiO_2-CaO-P_2O_5 based bioactive glasses were synthesized by the sol-gel method using calcium L-lactate pentahydrate and calcium nitrate tetrahydrate (CaNT) as calcium oxide precursors in order to achieve an improvement of the material bioactivity. The obtained samples were characterized by X-ray diffraction (XRD), FT-IR spectroscopy and scanning electron microscopy, then they were assessed from the perspective of their bioactive properties, while the textural properties were evaluated by Brunauer-Emmett-Teller method. The XRD pattern confirms the amorphous structure for all samples, except the glass synthesized with CaNT, where few crystallization centres associated with apatite phase were identified. A higher specific surface area and pore volume were obtained for the glasses prepared with calcium L-lactate pentahydrate in comparison with those obtained by using CaNT, result that was expected to be favorable in terms of bioactivity. The *in vitro* bioactivity assessment revealed the occurrence of a more pronounced apatite layer onto the glass' surfaces prepared with calcium L-lactate pentahydrate than as for the samples obtained with CaNT.

1. Introduction

A biomaterial is a substance designed to take a form that is used to direct the course of therapeutic or diagnostic procedures *via* control of interactions with the components' of the active system [1]. Biomaterials seem to solve the inconveniences of implants that show structural degradation or an immune response [2]. Bioactive glass is one of the most promising biomaterials and one of the only entirely synthetic materials that bind to the bone [3, 4]. The original Bioglass® was prepared by melt quenching method, obtaining a fully dense material, but this property limits their application in medicine [5]. By the appearance of sol-gel method, which permits the obtainment of porous materials, the applicability of bioactive glasses is much extended [6, 7]. Thus, the high specific surface area is the critical parameter in sol-gel derived bioactive glasses, which strongly depends on the dissolution rate and the increased bioactivity. The textural properties are based on the gelation time, calcinations temperature, glass composition and the precursors used [8–10]. In the nitrate-free sol-gel process, instead of calcium nitrate tetrahydrate (CaNT), which is the most used precursor for calcium oxide, other various precursors were used, such as calcium carbonate [11], calcium L-lactate pentahydrate [10] and calcium acetate [9], leading to different specific surface areas and pore volume. For example, using calcium carbonate, a specific surface area of 80.1 m^2/g has been obtained [11], while in the case of calcium L-lactate pentahydrate, the specific surface area was of 11.75 m^2/g and the pore volume of 0.065 cm^3/g [10]. Kumar et al. [9] had obtained better textural properties using calcium acetate, i.e., 522 m^2/g for the specific surface and 0.3771 cm^3/g for the pore volume. In these nitrate-free sol-gel processes instead of the nitric acid, the lactic [10], formic and acetic acid [9] were used. After a literature survey, it was found that Rezabeigi et al. [10] prepared 45S5 Bioglass®, by the sol-gel route using calcium L-lactate pentahydrate as calcium oxide precursor, yet the bioactivity of the materials was not evaluated.

The present work aims to highlight the influence of calcium L-lactate pentahydrate hydrolysed in the presence of nitric acid on the textural properties and bioactivity. Such materials are meant to replace the bone structure and to stimulate its formation, as the presence of the hydroxyapatite layer is evidenced [1]. Thus, it was prepared glasses with $62SiO_2{\cdot}30CaO{\cdot}8P_2O_5$ (mol%) composition knowing that they have excellent bioactivity and good biological response [12, 13]. In order to assess the bioactivity of the obtained samples, *in vitro* analyses were performed, before and after immersion in simulated body fluid (SBF),

* Correspondence to: K. Magyari, Nanostructured Materials and Bio-Nano-Interfaces Center, Interdisciplinary Research Institute on Bio-Nano-Sciences, Babeș-Bolyai University, M. Kogalniceanu 1, 400084 Cluj-Napoca, Romania.
** Correspondence to: L. Baia, Faculty of Physics, Babes-Bolyai University, M. Kogalniceanu 1, 400084 Cluj-Napoca, Romania.
E-mail addresses: klara.magyari@ubbcluj.ro (K. Magyari), lucian.baia@phys.ubbcluj.ro (L. Baia).

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Table 1
Codes of the investigated samples.

Sample code	Precursors of CaO component	Precursors of CaO component dissolved in	Hydrolyzed in presence of
G-CaNO-et	$Ca(NO_3)_2{\cdot}4H_2O$	Absolute ethanol	HNO_3
G-Ca-LL-et	calcium L-lactate pentahydrate	Absolute ethanol	HNO_3
G-Ca-LL-w	calcium L-lactate pentahydrate	Distilled water	HNO_3

by X-ray diffraction (XRD), Fourier Transformed Infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM).

2. Materials and methods

2.1. Glass formation

The $62SiO_2{\cdot}30CaO{\cdot}8P_2O_5$ (mol%) glasses were prepared by sol-gel method. The precursors used were tetraethyl orthosilicate (TEOS), triethyl phosphate (TEP), calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) or calcium L-lactate pentahydrate, hydrolyzed in presence of nitric acid (Table 1).

Reactants were added consecutively after 1-h intervals, under continuous stirring. The solutions (*sol*) were poured into closed containers that were kept at room temperature until gelation (*gel*) was reached (2–10 days). The resultant gels were aged at room temperature for 3 days and then dried at 150 °C for 24 h. Material stabilization was carried out at 600 °C for 3 h. This temperature was determined by performing a differential thermal analysis on the dried gels, and has been chosen for the thermal treatment the temperature of 600 °C for which the unbounded water, nitrates, and all possible volatile decomposition products are removed [14]. Prior characterization, the obtained glass was milled 30 min, by hand, using Agate mortar and paste in order to get glass samples with similar granulation.

2.2. Assessment of the bioactivity

In order to evaluate the bioactivity, the obtained powders were immersed in SBF in closable conical polypropylene flasks placed in an incubator at a constant temperature of 37 °C under static condition and analyzed after 7 days of immersion. The SBF was prepared according to Kokubo's protocol [15] and the solution was buffered at a pH of 7.4 at 37 °C. The weight of glass per volume of SBF used was 10 mg/mL for each sample. After 7 days, the powders were filtrated, rinsed several times with distilled water and dried.

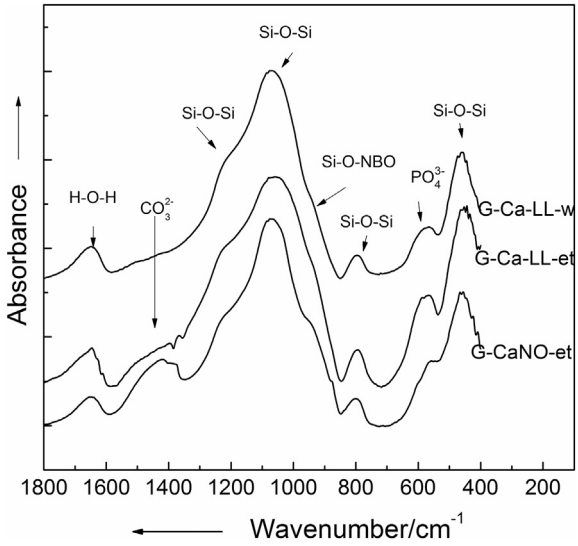

Fig. 2. FT-IR spectra of the *G-CaNO-et*, *G-Ca-LL-et* and *G-Ca-LL-w* glass samples.

2.3. Methods

2.3.1. X-ray diffraction

The X-ray diffraction analysis (XRD) was carried out on a Shimadzu XRD 6000 diffractometer using CuKα radiation (λ = 1.54 Å), with Ni-filter. The diffractograms were recorded in 2θ range from 10° to 80° with a speed of 2°/min.

2.3.2. FT-IR spectroscopy

The FT-IR absorption spectra were recorded in reflection configuration with a Jasco 6200 (Jasco, Tokyo, Japan) spectrometer, at room temperature, in the range 400–4000 cm^{-1}; spectral resolution of 4 cm^{-1}; using the well-known KBr pellet technique.

2.3.3. Specific surface area and pore volume

Textural properties were investigated with surface area analyzer Q surf Series M1. The surface area of the samples was determined by measuring nitrogen adsorption/desorption isotherms at 77 K, using the Brunauer-Emmett-Teller (BET) equation.

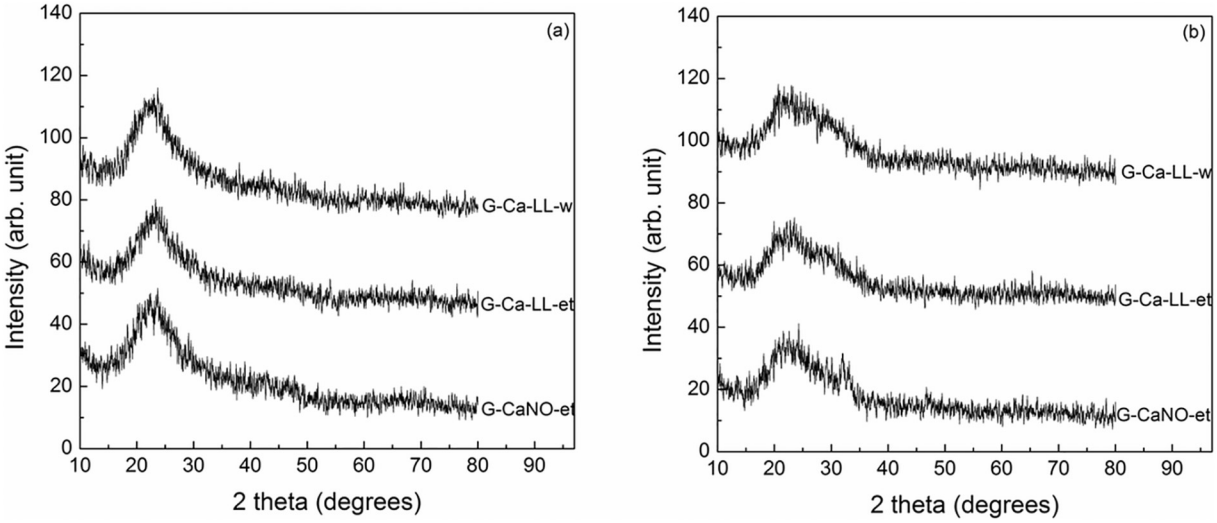

Fig. 1. XRD pattern for as prepared (a) and heat treated (b) *G-CaNO-et*, *G-Ca-LL-et* and *G-Ca-LL-w* samples.